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A Model of Low-Temperature Wafer Bonding And Its Applications

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ABSTRACT

Si–OH groups can polymerize to form strong covalent Si–O–Si bonds at low temperatures. Based on this behavior a model for hydrophilic Si wafer bonding is suggested which allows significant increase of bonding strength by low-temperature annealing. A possible extension of this model to materials other than Si is discussed. Methods to prevent generation of interface bubbles during the low-temperature annealing are presented. The low-temperature bonding approach has been employed in layer transfer applications such as an ultrathin silicon-on-insulator layers by an implanted carbon etch stop, single-crystal Si layer on quartz, glass, or sapphire. Analysis of thermal peeling stresses in bonded pairs of dissimilar materials led to the development of bonding and heating-cooling schedules as well as a low vacuum bonding method to avoid peeling during annealing and subsequent thinning (etching).

Introduction

Wafer bonding provides a high degree of flexibility in materials integration. Although differences of bonding materials in terms of composition, crystal structure, crystal orientation, wafer thickness, doping type, and profile do not present obstacles for wafer bonding, the thermal mismatch imposes a severe restriction on annealing temperature. The basic requirements for good bonding are: (*i*) the materials being bonded form a covalent or chemical bond across their interface, (*ii*) high stresses are avoided, and (*iii*) no interface bubbles develop. Usually these requirements can only be fulfilled via high-temperature annealing (typically at 1100°C or higher for Si) by bonding materials whose thermal expansion coefficients do not differ by more than 10%.[1] In order to fully exploit the potential provided by the wafer bonding approach, it is crucial to achieve strong bonding already by low-temperature annealing. The meaning of "low temperature" depends on the specific materials combinations, thickness of wafers involved, and the specific applications. Low-temperature bonding is also essential for bonding of processed wafers or compound materials to prevent undesirable changes or decomposition, even if the bonding wafers are thermally matched.

For strong bonds to occur, the two mating surfaces must be in sufficient proximity to allow the intermolecular forces to be effective. Two main methods are usually adopted to significantly increase the bonding area of pairs whose bonding surfaces are not perfectly smooth and flat:

(*i*) Elastic or plastic deformation of the original surface asperities when an external pressure is applied at elevated temperatures either through electrostatic forces, *e.g.*, in field-assisted metal/glass anodic bonding,[2] or via mechanical forces, such as in pressure-assisted metal/metal or metal/ceramic bonding.[3] However, the former depends on migration of mobile ions (*e.g.*, Na^+) from the glass driven by electrostatic and thermal forces. The latter generally cannot form a good bond unless high-temperature diffusion occurs.

(*ii*) A layer with a low melting or softening or diffusion temperature, such as a glass or a polymer or a palladium layer, or a metal layer whose eutectic temperature with the bonding substrate is low may be used as an intermediate layer at the bonding interface. A spin-on thin intermediate sodium silicate or aluminum-phosphate layers were used for Si/Si bonding which showed surface energy greater than 2000 mJ/m^2 after 200 or 350°C annealing,

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respectively.[4] However, the reliability, stability, and thermal stress concerns associated with the intermediate layer prevent wide acceptance of this method except for special applications.

A strong bond could also be realized at low temperatures if the bonding surfaces are perfectly clean, such as in an ultrahigh vacuum (UHV) system, and a sufficiently large area is in real contact at the bonding interface where the short-range dispersion or other intermolecular attraction forces between the atoms of mating surfaces become sufficiently large and bonding for almost all materials appears to be possible. Although first promising results of large area, self-propagating, room temperature bonding of 4 in. Si wafers in UHV have been obtained,[5] this method may be quite expensive and further investigations are required.

Based on the fact that strong bonds can be achieved through a long annealing at low temperatures at hydrophilic Si/Si bonding interfaces,[6] a model of hydrophilic Si wafer bonding is suggested. Possible applications of the model to materials other than Si are discussed. Using standard polished Si wafers, a strong bonding can be realized by 150°C annealing. Methods to prevent interface bubble generation during annealing are reported, and typical bonding processes for layer transferance of dissimilar materials are discussed.

A Model of Hydrophilic Si Wafer Bonding

A measure of the bonding strength of a bonded pair is the specific surface energy of one of the bonding wafers when the bonded wafers are partially separated by inserting, *e.g.*, a razor blade into the bonding interface. Although this procedure is usually performed in air, one should be aware that a reduction of the surface energy after separation due to adsorption of water or other molecules from the ambient is possible.

The surface energies of both bonded hydrophilic and hydrophobic pairs are functions of time as well as of temperature. At a given temperature, the surface energy increases with time and gradually approaches a stable value (saturated value) after a period of time. Therefore, the saturated values of surface energy should be used in any discussions unless specifically indicated. Figure 1 shows typical experimental results of the saturated surface energy of a hydrophilic Si/Si pair as a function of temperature. The bonded wafers were 4 in., Si(100) commercially available, prime-grade polished wafers. The mean surface microroughness was 1 Å. The surface hydrophilicity was realized by a cleaning and activation treatment in RCA solution. The hydrophilic Si surfaces are covered with a thin (native) oxide layer which is grown during wafer cleaning. From Fig. 1 it is clear that the bonding process consists of four stages:

1. From room temperature to 110°C: slow fracture effect and interface water rearrangement.—At relative humidities of 50% or greater, there is more than one monolayer of hydrogen-bonded molecular water on Si–OH groups present on silica-like hydrophilic Si surfaces.[7] During room temperature bonding, the two wafers bond to each other via hydrogen bonding between adsorbed water molecules on the two surfaces. Since water triplets are more stable than three isolated water molecules or dimers, the linkage of three or more water molecules can form a bridge across the two bonding surfaces. Since the size of an OH group is about 1.0 Å and the distance between two hydrogen-bonded oxygen atoms in ice is 2.76 Å, the hydrophilic Si surfaces separated by up to ~10 Å can be bridged through the clusters of three hydrogen-bonded water molecules at room temperature, as indicated in Fig. 2. This implies that for successful hydrophilic Si wafer bonding, the mean surface microroughness should be lower than ~5 Å, and bonding should be performed at relative humidities greater than 50%. This also applies to bonding of hydrophilic Si/SiO_2 and SiO_2/SiO_2 pairs. Therefore, bonding of hydrophilic wafers whose surface is not perfectly smooth and flat is feasible with the help of water bridging.

The surface coverage of molecular water on silica surfaces depends on relative humidity (RH), but even at 1.2% RH there is still a 0.24 monolayer coverage.[7] The bonding strength between vitreous silica surfaces was found to decrease when bonding was performed at RH<15% due to reduction of water coverage.[8] Water still remains at the surface after thermal treatment, even at 110°C in air if the air is humid.[9] All or most of the molecular water can only

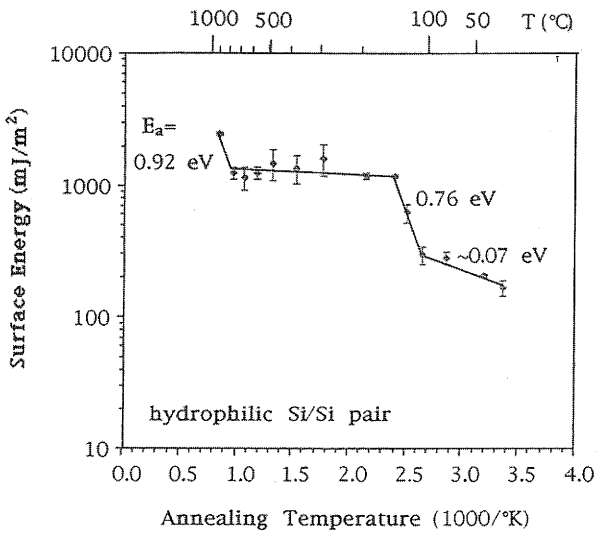

Fig. 1. Typical saturated surface energy of hydrophilic Si/Si pair as a function of annealing temperature.

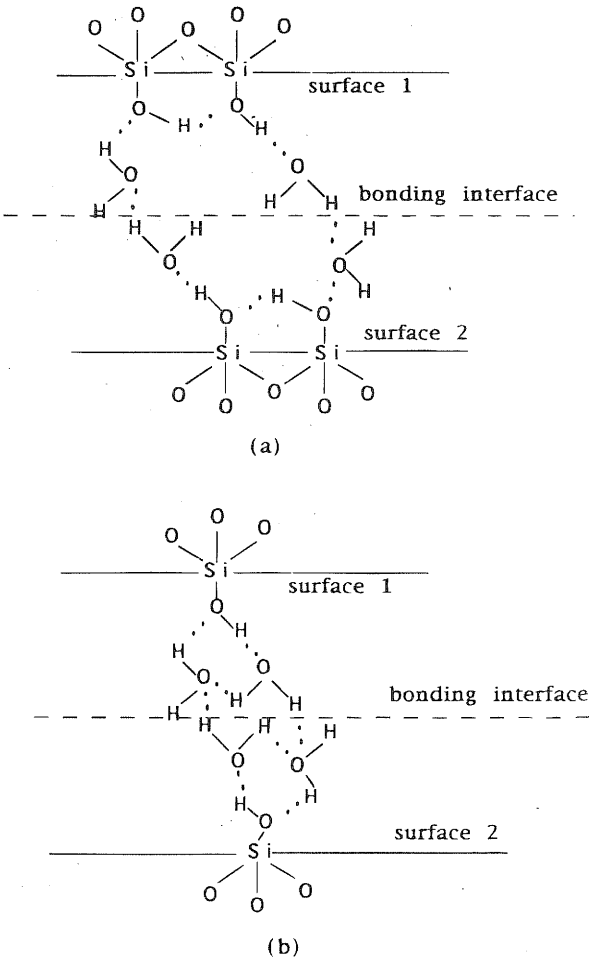

Fig. 2. Schemes of water bridging between two hydrophilic Si bonding wafers on (a) isolated, and (b) associated Si-OH groups.

be removed from silica surfaces upon heating above about 120°C in air.[8-10] If the relative humidity in the environment is larger than 15%, the molecular water at the interface of hydrophilic Si/Si pairs is expected not to change significantly during annealing in the temperature range from room temperature to 110°C. Since a mobile film structure exists at this stage,[7] the main interface reactions in this temperature range should therefore be: (*i*) the slow fracture effect of Si–O–Si bonds on both bonding surfaces via attack by the interface water,[10] *i.e.*

$$\text{Si–O–Si} + \text{HOH} \rightarrow \text{Si–OH} + \text{HO–Si} \qquad [1]$$

which leads to an increased number of OH groups extending from the surfaces into the interface region and thus to more hydrogen bonds across two mating wafers. (*ii*) Rearrangement of the interface molecular water to form more stable hydrogen-bonded structures.

The reactions are expected to be both time and temperature dependent. There is an increased silanol density at the bonding interface, and thus an enhanced bonding strength results. Figure 3 shows the measured surface energy of hydrophilic Si/Si, Si/SiO_2, and SiO_2/SiO_2 pairs as a function of time at room temperature. Because the chemical reactivity of the strained native oxide on Si is higher than that of the less strained thermal oxide, the surface energy immediately after bonding is higher for the former than the later. However, since the saturated silanol density for silica is 4.6/nm^2, *i.e.*, 4.6×10^{14}/cm^2, [11] all three bonding structures should show almost identical saturated surface energy if their surface smoothness, and therefore the area which is really in contact at their interfaces, is similar.

There are two main types of silanol groups on silica surfaces: isolated and hydrogen-bonded or associated OH groups.[1] The saturated density of isolated silanol groups is 1.4×10^{14} cm^{-2} and that of associated silanol groups is 3.2×10^{14} cm^{-2}. [1] As shown in Fig. 2, one isolated silanol group adsorbs two water molecules while a hydrogen-bonded associated silanol pair is needed to bind the same number of water molecules. The specific surface energy, γ, of a room temperature-bonded hydrophilic Si/Si pair may be approximately estimated as follows

$$\gamma = \frac{1}{2}(2d_{\text{OHi}}E_{\text{hi}} + d_{\text{OHH}}E_{\text{hH}}) \qquad [2]$$

where d_{OHi}, d_{OHH}, and E_{hH}, E_{hi} are the surface density and the hydrogen bond energy for the isolated and the associated silanol groups, respectively. If we use: $d_{\text{OHi}} = 1.4 \times 10^{14}$ cm^{-2}, $d_{\text{OHH}} = 3.2 \times 10^{14}$ cm^{-2}, $E_{\text{hi}} = 10$ kcal/mol $= 7 \times 10^{-17}$ mJ/hi-group, and $E_{\text{hH}} = 6$ kcal/mol $= 4.2 \times 10^{-17}$ mJ/hH-group, we obtain $\gamma = 165$ mJ/m^2.

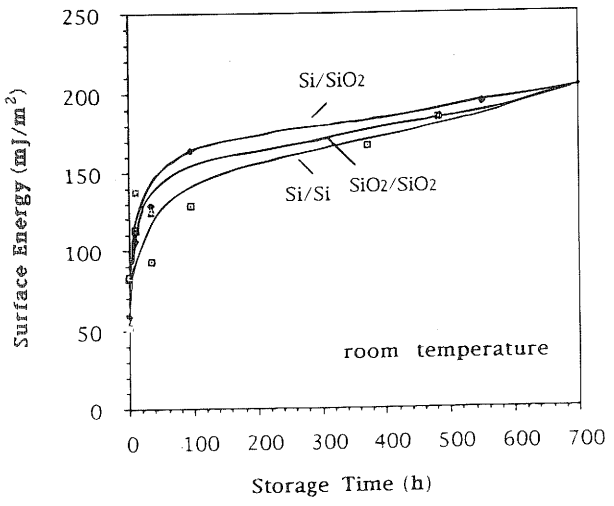

Fig. 3. Surface energy of hydrophilic Si/Si, Si/SiO_2, and SiO_2/SiO_2 pairs as a function of time at room temperature.

The calculated value of 165 mJ/m^2 is somewhat less than the measured saturated value (≥240 mJ/m^2) of the surface energy of room temperature-bonded hydrophilic Si/Si, Si/SiO_2, and SiO_2/SiO_2 pairs but in the correct order of magnitude.

As temperature increases, the water molecules gain increased surface mobility to form energetically more favorable structure. The added stability[12] of the new structure is in the range of 0.05 eV, which is consistent with the experimentally observed activation energy 0.07 eV of γ in this temperature range, as shown in Fig. 1.

2. From 110°C to 150°C: polymerization of silanol groups across the interface.—It is known that polymerization of silanol groups can take place at temperatures as low as room temperature when they are in close proximity and are hydrogen-bonded[8]

$$\text{Si–OH} + \text{HO–Si} \underset{k_r}{\overset{k_f}{\rightleftarrows}} \text{Si–O–Si} + \text{H}_2\text{O} \qquad [3]$$

It implies that if the interface molecular water can be removed, the silanol bonds which are hydrogen bonded between opposite surfaces should be transformed into strong siloxane bonds. The above reaction is reversible at $T < 425$°C if water is present. For the siloxane bridges to form across the bonding surfaces, excess water has to be removed. Since the molecular water can desorb from the wafer surfaces at above 110°C independent of air humidity, the interface is drying gradually during annealing at >110°C. Presumably, most of the molecular water diffuses along the bonding interface to the outside, but it cannot be excluded that some water molecules may diffuse through the surrounding native oxide and react with Si to form SiO_2 and hydrogen.

Reaction 3 may be described by a temperature-dependent equilibrium constant $K(T)$ given by

$$K(T) = \frac{k_f}{k_r} = \frac{[\text{Si-O-Si}]\,[\text{H}_2\text{O}]\text{s}}{[\text{Si-OH}]^2} \qquad [4]$$

where the brackets [ ] indicate concentration values. Since most physisorbed water has been removed, the molecular water at the interface $[H_2O]_s$ is generated by the polymerization reaction at >110°C. After a sufficiently long annealing at a given temperature, an equilibrium of water vapor pressure between the interface of a bonded pair and the outside can be established. This pressure increases probably somewhat away from the rim toward the center. Since the water vapor pressure outside the bonded pairs can be considered to be almost constant, the concentration of molecular water on the bonding surfaces $[H_2O]_s$ decreases exponentially with temperature. The equilibrium constant for the reaction between silicate glass and water is constant up to 300°C and increases at temperatures higher than 400°C.[13] We assume that the same is true for reaction 3. Therefore, the concentration of the interface siloxane bonds [Si–O–Si] should increase exponentially with temperature over the temperature range from 110 to 150°C, as long as the Si–OH density has not yet changed considerably

$$\gamma \propto [\text{Si-O-Si}] = \frac{K(T)[\text{Si-OH}]^2}{[\text{H}_2\text{O}]\text{s}} \qquad [5]$$

where γ is known from experimental results to be

$$\gamma = 2 \times 10^{12} \exp(-0.76/kT)\ \text{mJ/m}^2 \qquad [6]$$

3. From 150 to 800°C: bonding strength limited by contacted area.—For bonded standard Si/Si pairs, the saturated surface energy reaches ~1200 mJ/m^2 at 150°C and an almost constant surface energy is observed from 150 up to 800°C (see Fig. 1). It was reported[7] that water adsorption

on a quartz surface outgassed at temperatures in excess of 150°C is irreversible and the rehydration of the quartz surface is not complete from the vapor phase at low relative vapor pressure. We believe that almost all silanol groups at the interface have converted to siloxane bonds at ~150°C. Since the bonding surfaces are never perfectly smooth, the area over which bonding really occurs (termed contacted area) is limited. Figure 1 suggests that the surface energy of the pairs has reached the value which is determined by the contacted area at the interface over which all silanol groups at the interface have converted to siloxane bonds. It is expected that the absolute values of the surface energy in the plateau of Fig. 1 may vary depending on both the area which is really in contact at the bonding interface and on the density of siloxane bonds on the contacted surfaces. This density is expected to be lower than that of siloxane bonds within SiO_2.

If all the bonding sites on the surfaces are in contact, the surface energy in this temperature range can be approximately estimated by

$$\gamma = \frac{1}{2}(d_{OH}E_{Si\text{-}O}) \quad [7]$$

where d_{OH} is the surface density of all silanol groups, which is $4.6 \times 10^{14}/cm^2$, and $E_{Si\text{-}O}$ is the energy of a siloxane bond (4.5 eV). From Eq. 7 we obtain $\gamma = 1674$ mJ/m^2, which is consistent with the experimental observation. We mention again that this value depends on the actual density of silanol groups originally present on the surface and on the assumption that no additional water molecules attach to the surfaces after separation during the crack-opening measurement.

4. From 800°C and up: complete bond via oxide flow.—It is known that native oxides grown during wet chemical cleaning is a strained hydrous oxide with internal OH groups near the surface. It was also reported that the SiO_2 viscosity is greatly reduced when the SiO_2 contains H_2O. [14] For hydrophilic Si/Si pairs, the 800°C anneal may be sufficient to form siloxane bonds and to increase the contacted area at the interface by means of viscous flow of the native oxide, which can fill up the interface microgaps.[15] For Si/SiO_2, especially for SiO_2/SiO_2 pairs involving thermal oxide, which is less strained and has lower water concentration, annealing at above 1000°C is believed to be necessary to introduce SiO_2 mass transport and viscous flow at the bonding interface.[15] It explains the ~200°C higher annealing temperature required for Si/SiO_2 and SiO_2/SiO_2 pairs than for Si/Si pairs to complete the bond between two wafers.

The surface energy of completely bonded hydrophilic Si/Si, Si/SiO_2, and SiO_2/SiO_2 pairs can be estimated by substituting the SiO_2 bond density in bulk SiO_2 for d_{OH} in Eq. 7. We can use the bond density on Si (100) surfaces of of d_{Si} of 1.355×10^{15} cm^{-2} as an approximate value of the SiO_2 bond density, and $\gamma = 4932$ mJ/m^2 is obtained, which is in good agreement with 4100 mJ/m^2 reported for vitreous silica glass.[8] This value holds for the case of no water molecules attaching to the surfaces after separation. Such a value may be obtained, *e.g.*, under vacuum conditions.

However, for typical conditions of crack opening under atmospheric pressure and in the presence of humidity, adsorption of water molecules at the separated wafer surfaces will lead to a decrease in the measured surface energy down to about 2000 mJ/m^2, [16] corresponding to the values measured by Maszara *et al.*[15] for bonded oxidized silicon wafers and by Ball and Payne for the cracking of quartz.[17]

Based on this model of bonding, it is clear that a strong bond of hydrophilic Si/Si, Si/SiO_2, and SiO_2/SiO_2 pairs can be realized at temperatures as low as 150°C after a sufficiently long annealing time.

Bubble Generation and Prevention

A workable low-temperature bonding technology should not only offer strong bonding at low temperatures, but also an interface which is free of bubbles after the annealing. Usually this is not a concern for hydrophilic Si/SiO_2 and SiO_2/SiO_2 pairs, since the open network of oxide is a sink for gases which are desorbed from the bonding surfaces during annealing, but it is a major obstacle for Si/Si bonding in which bubbles can be formed during storage at temperatures as low as room temperature.[6]

The main causes of the interface gas bubbles include:[18,6] (*i*) desorption of hydrocarbon contaminants from bonding surfaces, (*ii*) hydrogen generation via oxidation reaction between interface water and Si, and (*iii*) trapped air pockets.

Trapped air can be avoided through careful bonding procedures, and the interface water itself does not lead to hydrogen bubbles if no hydrocarbons are present as nucleation sites for the bubbles.[16] Therefore, the hydrocarbon contaminants are the most important cause of bubble formation during annealing. A prebonding annealing of wafers at 600 or 800°C in oxygen or argon, respectively, can remove all thermally unstable hydrocarbon contaminants which are responsible for bubble generation during subsequent annealing of bonding pairs. However, high-temperature prebonding annealing may not be feasible for wafers containing structures which will be effected by such high temperatures. It is also not practical for materials with low dissociation temperature such as GaAs.

The commonly used RCA1 solution is designed to remove organic contaminants by both solvating action of the ammonium hydroxide and oxidizing action of the hydrogen peroxide, but about 0.1 monolayer of hydrocarbon still remains on the surface,[19] which causes bubble generation during annealing at around 300°C. Moreover, since plastic wafer boxes made of Teflon (PFA, perfluoroalkoxy polytetrafluoroethylene) can increase the organic contamination, on the wafer surface at room temperature,[20] mainly by fluorinated hydrocarbons, it is possible that PFA wafer carriers used in 80°C RCA cleaning would leave more hydrocarbon residues on wafer surfaces than if a quartz carrier is used. Experimentally, much more bubbles were indeed observed after 150°C annealing for 2 h for wafers cleaned with a plastic carrier than using quartz wafer carriers.

We have found recently, that complete removal of thermally unstable hydrocarbons from Si surfaces can be realized by treating Si wafers before bonding in a very strong 99.999% oxidizer-periodic acid (H_5IO_6) solution at a temperature of 100°C following RCA cleaning.[21,22] No bubbles could be observed after annealing at any temperature. It is expected that this cleaning solution could also be used for prebond cleaning of other materials. Detailed results are given by Tong *et al.*[22]

Applications of Low-Temperature Bonding

The low-temperature bonding approach has been employed in realizing bulk quality ultrathin silicon-on-insulator (SOI) layers by an ion-implanted carbon etch stop layer[23] and single-crystal ultrathin Si on quartz[24] or on glass.[25] Here the layer transferring by SOI/quartz bonding to realize single-crystal thin Si layer on quartz is used as an example to demonstrate the process design.

Let us assume that the difference in thermal expansion coefficients, $\Delta\alpha$, is independent of temperature (2.56×10^{-6}/°C for Si and 0.5×10^{-6}/°C for fused quartz). We also assume that no debonding or sliding occurs during operation. The boning pair has the following material parameters: E_1 and E_2 are Young's modulus of quartz and Si, respectively, d_1 and d_2 are the respective wafer thicknesses, ν_1 and ν_2 are the respective Poisson ratios, and R is the radius of the wafers. From elastic bimetallic strip theory,[26] in addition to the normal stresses (tension and compression) of the two bonding wafers that are parallel to the bonding interface, shearing stresses, and peeling stresses (vertical to the bonding interface) are also present. The shearing and peeling stresses are concentrated near the edges of the bonding pair and vary exponentially along the interface from the center ($x = 0$) to the edges ($x \cong R$). The shearing stresses τ can be expressed by the formula

$$\tau = \tau_{max} \exp [-k(R-x)] \quad [8]$$

where $\tau_{max} = \Delta\alpha\Delta T / \sqrt{\lambda k}$

$$\lambda = \left(\frac{1-\nu_1^2}{E_1 d_1} + \frac{1-\nu_2^2}{E_2 d_2} + \frac{3(d_1 + d_2)^2 (1-\nu_1^2)(1-\nu_2^2)}{E_1 d_1^3 (1-\nu_2^2) \quad E_2 d_2^3 (1-\nu_1^2)} \right) \quad [9]$$

$$k = \frac{2d_1(1+\nu_1)}{3E_1} + \frac{2d_2(1+\nu_2)}{3E_2} \quad [10]$$

The peeling stresses have a similar expression

$$p = p_{max} \exp [-k(R-x)] \quad [11]$$

where $p_{max} = \mu k \tau_{max}$

$$\mu = \frac{1}{2} \frac{E_1 d_1^3 d_2 (1-\nu_2^2) - E_2 d_2^3 d_1 (1-\nu_1^2)}{E_1 d_1^3 (1-\nu_2^2) + E_2 d_2^3 (1-\nu_1^2)} \quad [12]$$

Equations 8 to 12 are essentially the same as those derived by Suhir in Ref. 26.

In order to avoid debonding of the severely thermally mismatched Si/quartz pairs during annealing, according to Eq. 8 and 11 a low ΔT must be used, since all other relevant material parameters are fixed. In this respect, the initial bonding at a temperature, T_i, higher than room temperature will help to reduce the shear and peeling stresses at the interface at annealing temperature T_a. In order to minimize the thermal stresses in the bonded pair at room temperature as well as at T_a, the optimal temperature for initial bonding, T_i, should then be

$$T_i = \frac{1}{2}(T_a - RT) + RT \quad [13]$$

Based on the bonding model, T_a has been determined to be 150°C. Therefore, T_i = 86.5°C is most desirable. Although there is a stress present in the contacting pairs when they are cooled down to room temperature, this hot-bonding schedule effectively alleviates the stress in the pairs during annealing at 150°C and prevents debonding. Moreover, the bonded pairs are in an almost stress-free state during 75°C KOH etching that in turn effectively reduces the possibility of KOH penetration into the bonding interface.

After room temperature bonding, tiny air pockets are usually trapped at the bonding interface, especially when the bonding surfaces are relatively rough, which can cause bubbles or debonding during subsequent annealing. A room temperature storage for ~100 h in air is recommended to allow the trapped air to diffuse out from the interface. Alternatively, bonding under low vacuum (~1 to 100 Torr) can be used.

In order to strengthen the bonds at the interface sufficiently to survive 150°C annealing, the initially bonded pairs were first annealed at 120°C for 45 h using 1°C/min ramping rate from room temperature. The low ramping rate has been found necessary for the bonding strength to increase so that debonding even at 120°C can be avoided. The temperature was increased to 150°C at the end of 120°C annealing and remained for 45 h. No debonding could be observed during the 150°C annealing. Finally, the pairs were stored at 100°C for 40 h to strengthen the bond at the edge of the pairs, which was the most stressed region during 150°C annealing. Figure 4 is a scheme of the heating and cooling schedules for Si/quartz bonding.

The Si substrate of the SOI wafer was thinned by a KOH etching process. The built-in stress caused by the presence of the buried oxide (BOX) layer would result in a greater deformation of the SOI wafer with a thinned substrate if it was separated from the bonding quartz wafer. Therefore, when Si was almost completely removed and vertical etching was almost stopped on the BOX layer, stress-enhanced lateral etching of Si–O–Si bonds, as well as the Si layer

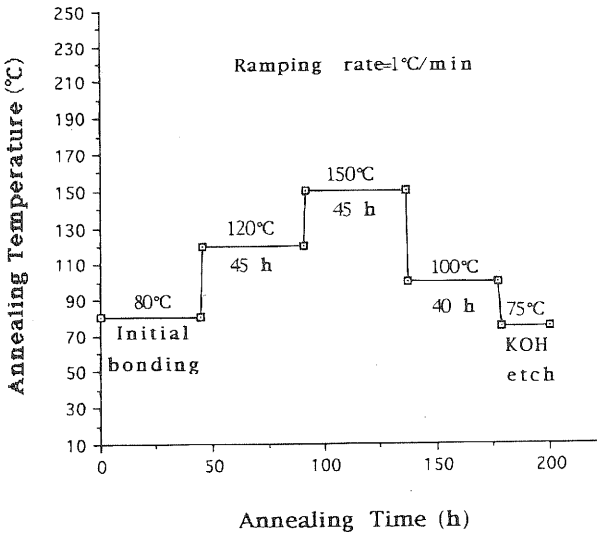

Fig. 4. Heating and cooling schedule for Si/quartz annealing.

along the interface, can become significant, especially for bonded wafers which had relatively rough surfaces.

The lateral etching rate along the bonding interface in 13.5% KOH aqueous solution at 75°C was found to be as high as 22-32 mm/h for annealed SIMOX (separated by implantation of oxygen)/quartz pairs. To alleviate the lateral etching problem, when the Si substrate of the SIMOX wafer was etched to about 100 μm thick, instead of using the KOH solution, EDP (ethylendiamine: pyrocatechol: water: pyrazine = 225 ml: 36 g: 30 ml: 1.35 g) was employed for the final etching at 100°C. Compared to KOH solution, EDP showed only 10 to 20% of the KOH lateral etching rate. Although the lateral etching differences between KOH and EDP could be attributed to factors like viscosity or diffusivity of the liquids, the dominant mechanism is believed to be the much smaller silicon oxide etch rate of EDP, which is about 10 to 15% of that in KOH at the etching temperature used. For BGSOI (bonded and ground-back)/quartz bonded pairs, EDP is usually not needed due to the smoother SOI surface. However, for SIMOX/quartz and SIMOX/glass the use of EDP as a final etchant is essential.

The low-temperature bonding process may also be applied to bonding of wafers with Si-based materials such as SiC, Si_3N_4, silicate glasses, provided a layer of SiO_2 is present on the surface of these materials. In the case of SiC or Si_3N_4, formation of an SiO_2 layer requires oxidation.

Generally speaking, it appears that any material that can form H–F, H–O, or H–N bonds, or that can attach electrophilic hydrogen on its surface, can be bonded via hydrogen bonding at room temperature to the same or a different material with a surface containing a sufficient density of nonbonding electrons on oxygen or nitrogen or fluorine, (Fig. 5), in addition to the basic requirements for bonding: the surfaces are sufficiently smooth, flat, and clean. Bonding surfaces covered with silicon oxide or

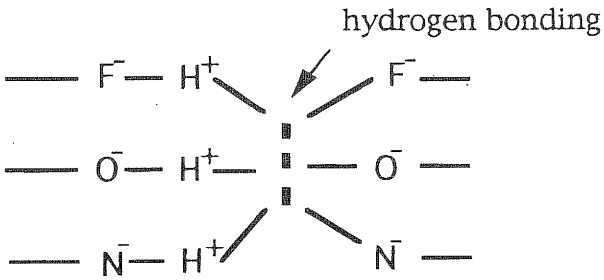

Fig. 5. Schematic diagram of hydrogen bonding.

nitride can form hydrogen bonding through activation treatments, mainly: (*i*) chemicals with OH^-, H^+, or F^- will attack a strained Si–O–Si or Si–N–Si bond to form Si–OH, Si–F, or Si–NH groups (Fig. 6), (*ii*) plasma treatment can introduce bond defects to enhance the chemical reactivity.

It was reported[27] that Si–NH groups can be formed on Si_3N_4 surfaces by an HF dip or NH_3 plasma treatment followed by a water rinse. Similar to Si–OH groups on Si surfaces, Si–NH groups across two bonding surfaces can also react to form strong bonds at temperatures as low as 90°C

$$Si–NH + HN–Si \rightarrow Si–N–Si + H_2 \quad [14]$$

For some metals, M, with relatively high electronegativity, such as those in group III or higher and some transitional metals, their oxides show less ionic character and their hydroxides may also be able to polymerize at low temperatures to form a stronger bond

$$M–OH + HO–Si \rightarrow M–O–Si + HOH \quad [15]$$

or

$$M–OH + HO–M \rightarrow M–O–M + HOH \quad [16]$$

Figure 7 shows the surface energy of an oxidized Si/sapphire (Al_2O_3) bonded pair as a function of annealing time at 150°C. It is believed that the polymerization effect is responsible for the increase of the bonding strength

$$Al–OH + HO–Si \rightarrow Al–O–Si + HOH \quad [17]$$

A similar reaction may also be involved in Si/ZnS bonding[28]

$$Zn–OH + HO–Si \rightarrow Zn–O–Si + HOH \quad [18]$$

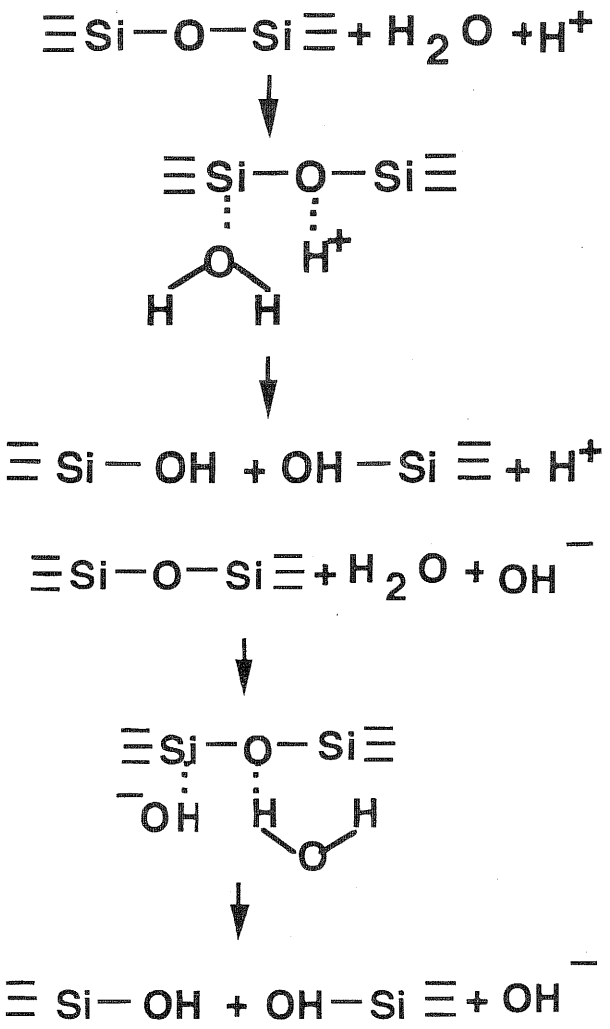

Fig. 6. The effect of H^+ (a, top) and OH^- (b, bottom) during the hydrophilization process.

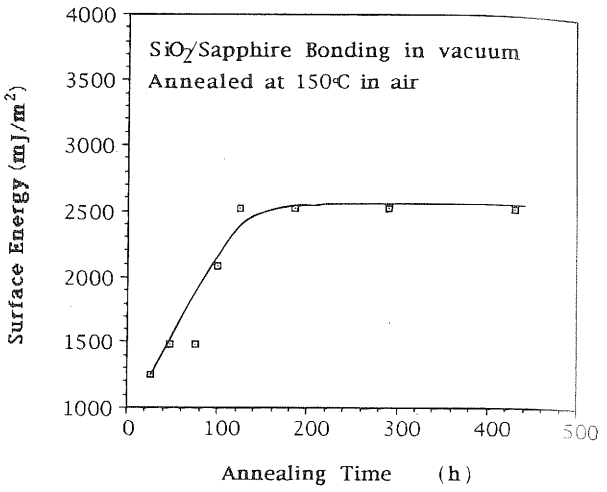

Fig. 7. Surface energy of a hydrophilic Si/sapphire pair as a function of time at 150°C.

Conclusions

1. Based on the fact that Si–OH groups can polymerize to form strong covalent Si–O–Si bonds at low temperatures, a four-stage hydrophilic Si wafer bonding model has been suggested.

2. The model may also be applicable to bonding of wafers with materials whose surface consists of SiO_2 or Si_3N_4 or some metal oxides (metals in group III or higher or some transitional metals). A strong bond can be formed during annealing at low temperatures such as 150°C.

3. Instead of a 600 or 800°C prebond annealing in O_2 or Ar, a simple chemical wet cleaning using the strong oxidizer H_5IO_6 can prevent bubble generation at the bonding interface during annealing.

4. Low-temperature bonding is essential for dissimilar material bonding. Analysis of thermal peeling stresses in bonded pairs of dissimilar materials led to the development of hot initial contacting and stepped heating-cooling schedules, as well as the low vacuum bonding method, to avoid peeling during annealing and subsequent thinning by etching.

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